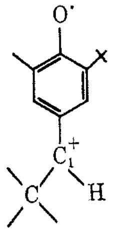
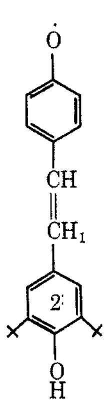
of triplets, located at the extrema of the spectrum and which are 33.6 gauss apart, belong to the 2,6-di-*t*-butyl-4-methyl phenoxyl radical.[12] This is a quartet of triplets with splittings of 11.2 and 1.67 gauss and a line width of 0.53 gauss and is referred to as spectrum "C." Thus, Figure 3 is comparable to a computer simulated spectrum with relative concentrations A/B/C of 3.5/1.1/1. Figure 3 leaves no doubt that the phenoxyl radical is present even though its presence is difficult to explain except perhaps by the principle of microscopic reversibility. If one examines the spectrum shown in ref 1 it is apparent that, because of the poor signal-noise ratio, the "pair" of triplets was probably the two center triplets belonging to the phenoxyl radical.

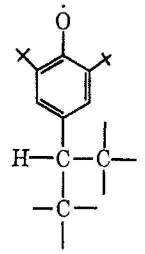
Therefore, it is unlikely that II is a radical intermediate in the decomposition of the quinone methide. Further difficulties arise when one inquires about the nature of II. Possibly more complete structures include VIII-X.



VIII



IX



X

If VIII, then C_1 is sp^3 and only ring hydrogens will contribute to hyperfine splitting (hfs).[12,13] If IX, then H_1 and ring (2) hydrogens will contribute to hfs. X would produce the "observed" hfs but such a structure is unlikely.

In summary, one concludes that spectrum A is always noted in the decomposition of the quinone methide. B and C are present occasionally but these are identified as radicals which are not likely to be primary participants. A may be identified as the partial structure I[1] which in turn may represent the three structures III, IV and IV. Esr cannot distinguish between these but in view of known reactions,[7,10] it is likely that all three are present.

Perhaps, it is worthwhile to report that spectrum A has also been recorded during the oxidation of the parent phenol. Figure 4 was recorded after 131 min of reaction with mercuric oxide in carbon disulfide solution. The components are unambiguously interpreted to be equal parts of A and C.

Experimental Section

Preparation of 2,6-Di-*t*-butyl-4-bromomethylphenol (XI).—2,6-Di-*t*-butyl-4-methyl-4-bromo-2,5-cyclohexadienone, prepared after Coppinger and Campbell,[14] was heated in an evacuated, sealed Pyrex tube for 10 min at 100°. The nmr spectrum of the product dissolved in carbon disulfide showed the OH and CH_2Br peaks at τ 4.89 and 5.64 and indicated complete conversion to the benzyl bromide.

4-Methylene-2,6-(Di-*t*-butylcyclohexa-2,5-dienone (Quinone Methide).—After Filar and Winstein,[15] equivalent amounts of XI and triethylamine in carbon disulfide were mixed in the absence of air and filtered into a Varian sample tube. The nmr sample tube was welded to one end of a medium porosity Pyrex filter tube and a 4-mm glass tube fitted with a syringe cap was welded to the other end. The benzyl bromide solution was added through the syringe cap and frozen with liquid nitrogen. The triethylamine solution was similarly added. The argon atmosphere, which was previously added, was evacuated with a vacuum pump and the 4-mm glass tube was flame sealed. The contents were allowed to melt, shaken for 1 min at approximately −10°, and filtered by cooling the nmr tube in a Dry Ice bath. Finally the contents were frozen in liquid nitrogen while the nmr tube was flame sealed. The nmr spectrum was similar to that reported in ref 10 and indicated quantitative conversion to the quinone methide. In the case of the more concentrated solution (0.25 *M*), the radical (Figure 1) appeared to be in a steady-state concentration for about 3 hr and finally tailed off to a negligible concentration after 4 hr.

Oxidation of 2,6-Di-*t*-butyl-4-methylphenol (XII).—The mixture (0.0060 g of XII, 0.0250 g of mercuric oxide, and 0.18 ml of carbon disulfide) was sealed in a 4-mm Pyrex tube and examined in the esr spectrometer at 102° over a period of 24 hr. A similar mixture was prepared for nmr mesurements using the filtreing device described above. After 24 hr at 100° the hot mixture was filtered into the nmr tube. There was no precipitate formed after cooling to room temperature. The nmr spectrum of the filtrate showed the filtrate to be two parts VI and one part VII.

Instrumental.—The nmr[16] and esr[17] have been previously described.

Acknowledgments.—The author wishes to thank Dr. E. B. Baker for the use of the nmr spectrometer as well as Professor Earl Huyser and Dr. Corwin Bredeweg for helpful discussions. He also wishes to thank the reviewer for calling the work of Chandross and Kreilick[11] to his attention.

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A New Preparation of 4-(*p*-Tolyl)-1,2-dithiole-3-arylimines

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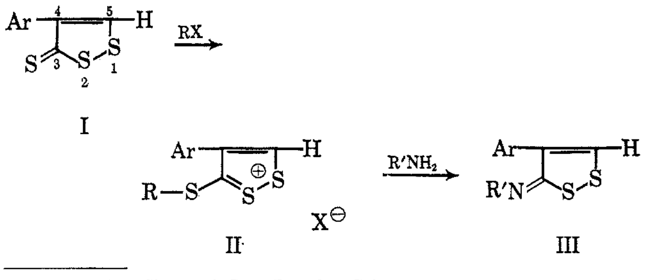
Trithionium salts (II), formed by the reaction of alkyl halides with 1,2-dithiole-3-thiones (I), react with amines to yield the 3-imines (III) and a mercaptan.[2a]



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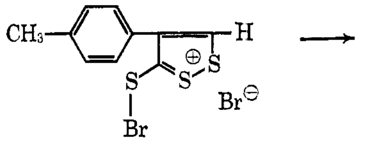
[1] Arapahoe Chemicals Inc., Boulder, Colo.

[2] (a) A. Luttringhaus and U. Schmidt, *Chem.-Ztg.*, **77**, 135 (1953); see *Chem. Abstr.*, **47**, 4836a (1953); (b) W. R. Diveley, K. Brack, and A. D. Lohr, *J. Agr. Food Chem.*, **12**, 251 (1964).

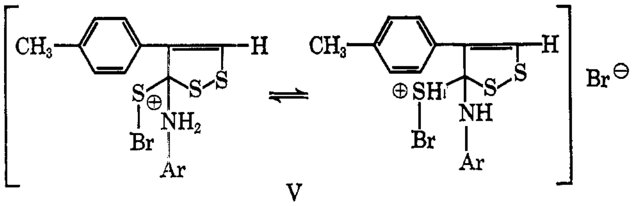
On the other hand, the 4-(p-tolyl)-1,2-dithiole-3-thione hydrobromide gave only trithione upon addition of aniline, and the trithione reacted very slowly with aniline in refluxing benzene solution. Direct refluxing with aniline opened the dithiole ring to provide materials that absorb in the 3.0-μ region.

The types of halogenated derivatives formed from trithiones depend on the solvent and the halogen. Chlorination in refluxing chloroform gives a 3,3,5-trichlorodithiole,[2b] whereas in acetic acid the 3,3-dichlorodithiole and a monochloro intermediate are formed.[3] Bromine and iodine trithione adducts have also been reported.[4]

In the work reported here, the room-temperature addition of 1 mole of bromine in carbon tetrachloride or benzene solution to 4-(p-tolyl)-1,2-dithiole-3-thione quantitatively precipitated a tan, high-melting solid. The solid did not absorb in the 8.9-μ region, evidence for reaction at the thiocarbonyl group. Isolation of trithione by aqueous acetic acid hydrolysis of the solid showed that the thione sulfur atom remained attached during the bromination. Reaction of the solid with primary aryl amines gave the 3-imines. Assuming that the solid is the bromotrithionium bromide IV, V was formed by addition of the amine. Loss of hydrogen bromide and sulfur yielded the imine hydrobromide. Aliphatic amines produced intractable tars.



IV



V

Experimental Section

Nuclear magnetic resonance spectra were measured at 52 Mc with a Varian Associates DP-60 spectrophotometer, with tetramethylsilane as internal standard.

4-(p-Tolyl)-1,2-dithiole-3-anil.—A solution of 2.24 g (0.010 mole) of 4-(p-tolyl)-1,2-dithiole-3-thione in 75 ml of carbon tetrachloride was treated with 1.70 g (0.0106 mole) of bromine dissolved in 25 ml of carbon tetrachloride. The tan solid that formed was collected, washed with carbon tetrachloride and pentane, and mixed with 10 ml of aniline; then ether was added. The ether-insoluble salt was collected and hydrolyzed with water, and the product was dissolved in benzene. The ether filtrate was diluted with pentane, and the small amount of solid that formed was collected and added to the benzene solution. The benzene was decolorized with Norit and concentrated. The addition of pentane produced 2.33 g (82%) of 4-(p-tolyl)-1,2-dithiole-3-anil: mp 139–141°, yellow-orange crystals; nmr ($CDCl_3$), 8.18 (singlet, 1 proton), 7.39 (complex 9 aromatic protons), and 2.34 ppm (singlet, 3 methyl protons); nmr for 4-(p-tolyl)-1,2-dithiole-3-thione (CCl_4), 8.26 (singlet, 1 proton), 7.28 (*para*-substituted aromatic, 4 protons), and 2.41 ppm (singlet, 3 methyl protons).

Anal. Calcd for $C_{16}H_{13}NS_2$: C, 67.80; H, 4.62; N, 4.94; S, 22.6. Found: C, 67.61; H, 4.57; N, 48.3; S, 22.9.

4-(p-Tolyl)-1,2-dithiole-3-benzylimine.—The trithione dibromide was prepared by addition of 4.89 g (0.0305 mole) of bromine in 30 ml of benzene to 6.72 g (0.030 mole) of the trithione in 120 ml of benzene. The crude dibromide was washed with benzene and treated with 11 ml of benzylamine. After the exothermic reaction had subsided, ether was added and the insoluble salt was collected and thoroughly washed with ether. The salt was hydrolyzed with water and the imine was dissolved in benzene and crystallized from benzene–hexane to yield 4.65 g (52%) of 4-(p-tolyl)-1,2-dithiole-3-benzylimine: mp 111–113°; nmr ($CDCl_3$), 7.91 (singlet, 1 proton), 7.31 (complex, 9 aromatic protons), 4.87 (singlet, 2 methylene protons), and 2.31 ppm (singlet, 3 methyl protons).

Anal. Calcd for $C_{17}H_{15}NS_2$: C, 68.64; H, 5.08; N, 4.71; S, 21.6. Found: C, 68.67; H, 5.44; N, 4.60; S, 21.8.

4-(p-Tolyl)-1,2-dithiole-3-(p-carboxyphenyl)imine.—The dibromide prepared from 8.96 g (0.040 mole) of trithione was treated with 16.5 g of p-aminobenzoic acid dissolved in 200 ml of methanol. The mixture was stirred for 15 min and the solid that formed was collected and washed with methyl ethyl ketone, benzene, and hexane. The crude imine was dissolved in 250 ml of pyridine, decolorized with Norit, and crystallized by the addition of 650 ml of ether. The yield of 4-(p-tolyl)-1,2-dithiole-3-(p-carboxyphenyl)imine was 9.85 g (75%): mp 252–258° dec; λ_{max}^{mull} 6.00 and 6.25 μ.

Anal. Calcd for $C_{17}H_{13}NO_2S_2$: C, 62.35; H, 4.01; N, 4.28; S, 19.6. Found: C, 62.40; H, 3.92; N, 4.30; S, 19.5.

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4-Mercapto-5-(p-tolyl)-2H-thiapyrans

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4-Aryl-1,2-dithiole-3-thiones,[2a] readily available from the reaction of sulfur with the appropriate cumene or α-methylstyrene, are a source of a large number of new sulfur chemicals. 4-(p-Tolyl)-1,2-dithiole-3-thione (I) reacted with several active methylene compounds to provide high yields of orange or red compounds containing two sulfur atoms. Condensations were carried out at room temperature using sodium ethoxide in benzene–ethanol solution. Other condensing agents were also used. *E.g.*, malonic ester condensed in a dimethoxyethane–benzene solvent pair with sodium amide as the condensing agent. Ethyl cyanoacetate and the trithione condensed very rapidly in benzene solution when piperidine was added. Acetoacetic ester or ethyl benzoylacetate did not react but malononitrile condensed very readily. In these condensations both the methylene and ester or cyano groups are involved and sulfur is lost.

The addition of ethyl cyanoacetate to ethylene sulfide,[2b] gives an imino tetrahydrothiafuran existing as a mixture of tautomers. In a similar manner the addition of malonate ion to the trithione I caused cleavage of the dithioester to yield the intermediate III. Successive loss of sulfur, ring closure, and loss of ethoxide gave the 3-carbethoxy-4-mercapto-5-(p-tolyl)-2H-thiapyran-2-one (IV) in 86% yield. The 2-imino-2H-thiapyrans V and VI were obtained in 86 and 77% yield, respectively. (See Scheme I.)

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